Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

A NEW METHOD OF TRANSFORMING ESTERS OF α-AMINOACIDS INTO THEIR CORRESPONDING ISOTHIOCYANATES

By Treat B. Johnson and Arthur A. Ticknor

SHEFFIELD SCIENTIFIC SCHOOL, YALE UNIVERSITY

Communicated by L. B. Mendel, February 28, 1917

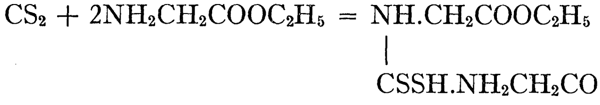
In a previous paper from this laboratory,[1] the writer called attention to the chemistry of polyketide mustard oils of the type $C_2H_5OOC.CHR.NCS$, and indicated the need of a practical method for preparing such combinations in quantity for synthetical work. This problem was undertaken by us and a method of synthesis was developed whereby isothiocyanates of the above type can be prepared directly from esters of α-aminoacids by subjecting the latter to the action of thiophosgene in dry toluene solution. For example, ethyl aminoacetate, in the from of its hydrochloric acid salt, interacts smoothly with thiophosgene in boiling toluene giving an excellent yield of the corresponding mustard oil—ethyl isothiocyanacetate. The transformation is expressed by the following equation: This reaction

$$CSCl_2 + HCl.NH_2CH_2COOC_2H_5 = 3HCl + SCN.CH_2COOC_2H_5,$$

has now been applied successfully in other cases and the results obtained will be published later in the *Journal of the American Chemical Society*.

While the above method of synthesis offers no difficulty so far as manipulation is concerned, it does involve in its application, however, the used of thiophosgene, which is an unpleasant reagent to work with and requires much time to prepare in quantity. We have now developed a method of operation whereby we are able to convert esters of α-aminoacids into their corresponding isothiocyanates without the use of this disagreeable reagent. In this preliminary note we record the principle of this method and its application for the preparation of ethyl isothiocyanacetate.

Emil Fischer[2] has shown that the ethylester of glycocoll interacts quantitatively with carbon-bisulphide in ether solution to form the dithiocarbamic acid salt represented by Formula I. The reaction is expressed by the following equation:



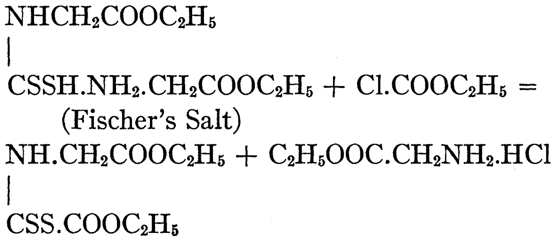
$$CS_2 + 2NH_2CH_2COOC_2H_5 = \begin{array}{l} NH.CH_2COOC_2H_5 \\ | \\ CSSH.NH_2CH_2COOC_2H_5. \end{array} \qquad (I)$$

As far as we are aware, this is the only ester of an α-aminoacid that has been coupled with carbon-bisulphide in this manner. Fischer attempted to convert this salt into ethyl isothiocyanacetate by digestion in aqueous solution with silver and mercury salts (Hoffmann's mustard oil reaction). He found that it underwent decomposition by such treatment giving solutions having the odor of a mustard oil, but ethyl isothiocyanacetate was not isolated by him.

We now find that this dithio carbamic acid salt I of Fischer's can be transformed easily and almost quantitatively into ethyl isothiocyanacetate by application of an unique reaction discovered by Andreasch.[3] This investigator has shown that simple amine salts of the above type interact with ethyl chloroformate at ordinary temperature giving smoothly isothiocyanates with evolution of carbonoxysulphide and ethylalcohol. The reaction is expressed by the following general equation:

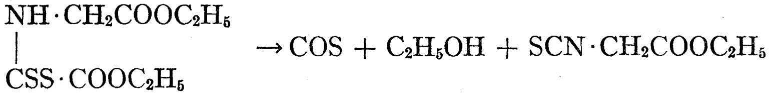
$$\mathrm{R.NH.CSSH.NH_2R. + ClCOOC_2H_5 = RNCS + COS + C_2H_5OH + R.NH_2.HCl}$$

Fischer's glycocoll-dithiocarbamic acid salt I also interacts with ethylchloroformate according to the above expression giving an intermediate thiolester having the Formula II. Therefore the first phase of this transformation may be expressed by the following equation:



$$\begin{array}{l} \mathrm{NHCH_2COOC_2H_5} \\ | \\ \mathrm{CSSH.NH_2.CH_2COOC_2H_5 + Cl.COOC_2H_5 =} \\ \quad \text{(Fischer's Salt)} \\ \mathrm{NH.CH_2COOC_2H_5 + C_2H_5OOC.CH_2NH_2.HCl} \\ | \\ \mathrm{CSS.COOC_2H_5} \end{array} \qquad \text{(II)}$$

This thiolester displays greater stability than combinations of this type, which have hitherto been described. Below 100° the ester II is quite stable. If heated above this temperature in a vacuum, it undergoes a smooth decomposition. Carbonoxysulphide is copiously evolved together with alcohol, and nearly a theoretical yield of ethyl isothiocyanacetate is produced. The mustard oil agrees in all its properties with the isothiocyanate prepared by the thiophosgene method, and boils at 102–104° at 10 mm. pressure. The second phase of this interesting reaction is expressed by the following equation:



$$\begin{array}{l} \mathrm{NH\cdot CH_2COOC_2H_5} \\ | \\ \mathrm{CSS\cdot COOC_2H_5} \end{array} \rightarrow \mathrm{COS + C_2H_5OH + SCN\cdot CH_2COOC_2H_5}$$

Starting with 35 grams of ethyl aminoacetate we recovered practically one-half of the aminoacid ester in the form of its hydrochloride, and obtained 19 grams of the isothiocyanacetate. This reaction is being investigated further and will be applied for the preparation of other new types of polyketide mustard oils. If this method of synthesis finds as wide an application as we anticipate, it will enable us to obtain several isothiocyanates of new types, which should be of great biochemical interest.

[1] Johnson and Hemingway, *J. Amer. Chem. Soc., Easton, Pa.*, **38**, 1916 (1550).

[2] Fischer, E., *Berlin, Ber. D. Chem. Ges.*, **34**, 1901 (441).

[3] Andreasch, *Wien, Monatshefte Chem.*, **27**, 1906 (1211).

THE GEOLOGY OF THE FIJI ISLANDS

By Wilbur G. Foye

DEPARTMENT OF GEOLOGY, MIDDLEBURY COLLEGE, MIDDLEBURY, VERMONT

Communicated by W. M. Davis, February 28, 1917

The period between July, 1915 and March, 1916 I spent as a Sheldon Travelling Fellow of Harvard University, in a study of the geology of the Fiji Islands. Special attention was given to the structure and relations of the elevated limestones. Of the larger islands, Viti Levu, Vanua Levu, Taviuni, Kandavu, Mbengha, and Ovalau were visited. Three islands of the Yasawa group and eighteen of the Lau group were likewise studied. The following paper records the principal facts concerning the geology of the major divisions of the group.

1. *Viti Levu.*—Viti Levu is the southern of the two larger islands of Fiji. It is 94 miles long from east to west and 55 miles broad. The southeastern side of the island and a large portion of the eastern and northeastern sides are low delta flats overgrown with mangrove bushes. The flats merge into a young, narrow coastal plain which extends 5 to 10 miles inland, where it meets an uplifted coastal plain of soft marls, now carved into mature hills, 70 to 100 feet in height. The older plain slopes gradually upward for 5 or 6 miles from its edge, until it rests unconformably on the interior, volcanic hills at heights of 600 to 700 feet. Elsewhere the volcanic hills approach the shore and form the coastline for the greater part of the circumference of the island.

The whole interior of the island is characterized by maturely dissected insequent hills, though quite extensive flats are sometimes found near the rivers. The rocks forming the interior hills are frequently sandstones and marls in contrast to the volcanic rocks of the coast. The western and northern shores of the island are very irregular. Drowned valleys abound and many are so filled with delta deposits that